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On the mechanism of electrochemical ion transfer reactions

O. Pecina, W. Schmickler, E. Spohr

Universität Ulm, D-89069 Ulm, Germany

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Abstract

The Gibbs energy curve experienced by an ion approaching the surface of a metal electrode is investigated by molecular dynamics using the I^- ion approaching a platinum electrode in an aqueous solution as an example. The maximum of the potential energy curve is determined by the partial desolvation of the ion before it is adsorbed. Electron exchange with the electrode does not occur at the maximum of the potential energy curve, but on the descending branch where the ion approaches the surface. A surface charge density on the electrode surface changes the potential energy curve both through the action of the resulting electric field and by changing the structure of the solvent near the surface. It is argued that ion transfer reactions differ in fundamental aspects from electron transfer reactions and cannot be interpreted in terms of the Marcus theory.

Keywords: Computer simulation; Ion transfer reactions; Gibbs energy; Molecular dynamics

1. Introduction

Electrochemical electron and ion transfer reactions are commonly interpreted using the same phenomenological Butler–Volmer law, according to which the rate constant for the anodic reaction depends on the temperature and the electrode potential in the following way:

$$k = A\ \exp\frac{-E^\circ_{\mathrm{act}}}{kT}\exp\left(\frac{z\alpha e_0\eta}{kT}\right) \tag{1}$$

where the pre-exponential factor A is independent of temperature and electrode potential, E°_{act} is the energy of activation at the standard equilibrium potential of the reaction, the overpotential η is the deviation of the electrode potential from the standard equilibrium value, the transfer coefficient α is a phenomenological constant of the order of $1/2$ and z is the number of electrons transferred ($z = 1$ for electron transfer reactions). At first glance this is no more than a phenomenological linear Gibbs energy relationship. However, closer inspection reveals a non-trivial aspect — the dual role played by the transfer coefficient which determines the dependence of the rate on both overpotential and temperature. This implies that the value of the transfer coefficient determined from the potential dependence of the rate must be independent of temperature.

In the case of outer-sphere electron transfer reactions the Butler–Volmer law rests on solid experimental and theoretical evidence. Experimental investigations such as those by Curtiss et al. [1] have shown that the transfer coefficient of simple electron transfer reactions is indeed independent of temperature. The theoretical basis is provided by the theories of Marcus [2] and of Levich and Dogonadze [3], which also predict deviations at high overpotentials which have been confirmed experimentally [4,5].

In contrast, the validity of the Butler–Volmer law for ion transfer reactions is doubtful. Conway and coworkers [6] have collected data for a number of proton and ion transfer reactions and have found a pronounced dependence of the transfer coefficient on temperature in all cases. These findings were supported by experiments conducted in liquid and frozen aqueous electrolytes over a large temperature range [7,8]. However, Krishtalik [9] has claimed that any apparent dependence of the transfer coefficient on temperature is caused by double-layer effects, a statement which is difficult to validate because double-layer corrections, in particular their temperature dependence, depend on an exact knowledge of the distribution of the electrostatic potential at the interface, which is not available. Similarly, Schwarz et al. [10] measured the rate of the reduction of bromate on mercury and found that the transfer coefficient was independent of temperature. However, the reduction of bromate is a complex reaction involving six electrons, and double-layer corrections played an important role in the evaluation of the data. Therefore the experimental situation is extremely controversial. Theoreti-

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cal treatments of ion transfer reactions are few, and are generally based on variants of electron transfer theory which is surprising in view of the different nature of the elementary act [11].

In this study we investigate by computer simulations the potential of mean force that an ion or atom experiences as it approaches an electrode surface. The resulting Gibbs energy curve must play an important role in any microscopic theory of ion transfer reactions. We compare our results with the potential energy surfaces obtained from Marcus-type theories for electron transfer reactions, and argue that electron and ion transfer at electrode surfaces differ in essential aspects.

Similar computer simulations for ensembles of water with one or two ions have been performed by a number of groups, but with different aims. We would like to cite the work of Glosli and Philpott [12] and of Xia and Berkowitz [13], who have adopted similar approaches.

2. The model system

We chose the transfer of an iodide ion from an aqueous solution to a single-crystal platinum (100) surface as our model system. The actual calculations are based on earlier work by Spohr [14,15], to which the reader is referred for details. Here, we briefly summarize the essential features of the model system.

Microcanonical molecular dynamics simulations were performed on an ensemble consisting of 304 water molecules plus one iodide ion or iodine atom sandwiched between two parallel platinum surfaces a distance of 25 Å apart. The water molecules were represented by the widely used TIP4P model [16]. The interaction potential between water and the platinum surface, and the platinum–platinum force field are the same as in Ref. [14]. The potentials for the interaction of the iodide ion with water and with the platinum surface [15] are based on the results of ab-initio calculations [17]. The interaction of the iodine atom with water was assumed to be the same as that of the iodide ion but without the Coulomb term, i.e. the atom was considered to be an uncharged ion.

The interaction of the iodine atom with the platinum surface is a more delicate point. While there are two different charge states in the solution (the atom and the ion), there is only one adsorbed state with a partial charge and a broadened electronic orbital [18,19] (Fig. 1). Therefore the potential energy curves for the atom and the ion coincide in the immediate vicinity of the surface, and diverge as the particle moves towards the bulk of the solution. Obviously, this situation is difficult to mimic in a simulation. We have simply taken the same interaction potential for the atom as for the ion, i.e. the iodide–platinum potential calculated by Seitz-Beywl et al. [20]. This potential is based on a quantum-chemical cluster calculation; it is relatively short-ranged, and image interactions are included in a summary fashion only. For these reasons that part of our calculated potential energy curve that is close to the platinum surface is not very reliable. Fortunately, it turns out that this is not important for the main point of this work, which deals with the energy barrier that is situated a few ångströms in front of the electrode surface.

The electrostatic interactions between the particles have been calculated by Ewald summation in two dimensions. Image charge terms have not been incorporated.

The potential of mean force was calculated from a constrained molecular dynamics simulation [21]. In this method the distance between the ion or atom and the center of mass of the platinum crystal is kept fixed, and the solvent-averaged mean force between the particle and the metal is obtained from the simulations. All simulations were performed for a temperature of 300 K.

3. Results and discussion

3.1. Results for an uncharged metal surface

The principal result obtained from the simulations is the mean force $F_s(z)$ exerted by the solvent on the solute as a function of the distance z from the metal surface, which is taken here as the center of the top layer of metal atoms. Fig. 2(a) shows our data for both the ion and the atom; note that these do not yet include the interaction with the metal, and that a negative force is directed away from the

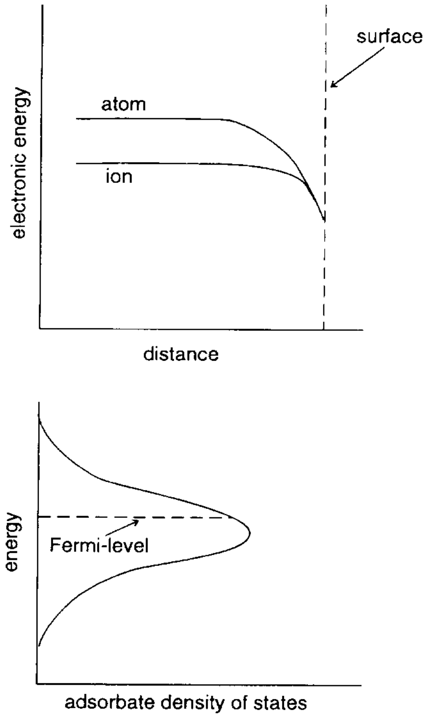

Fig. 1. (a) Electronic energies for the I^-–I system as a function of the distance from the metal; (b) density of states of the adsorbate (schematic).

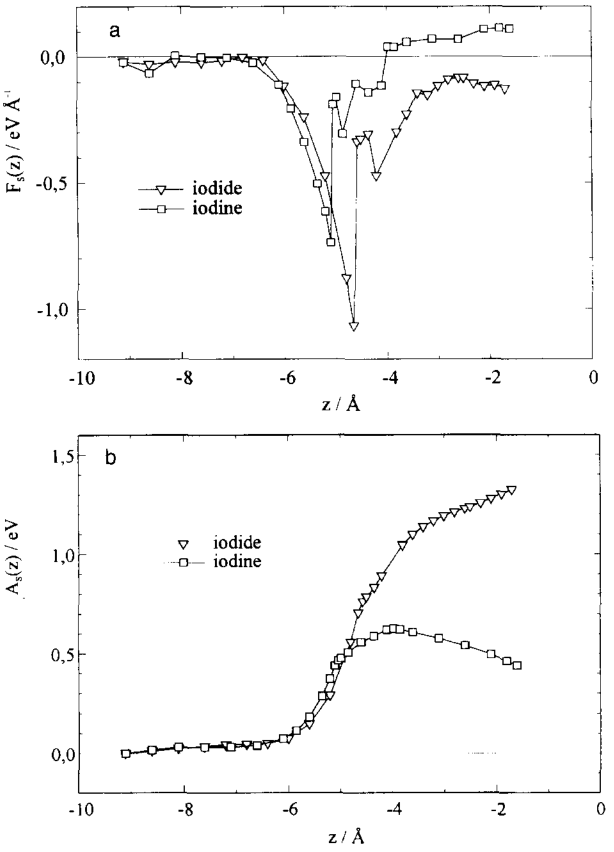

Fig. 2. (a) Mean solvent force and (b) corresponding Gibbs energy for I and I^- in the absence of an external field.

surface. The critical region is between 4 and 6 Å from the metal surface, and so we performed more simulations in this region than elsewhere. An extensive discussion of numerical errors is given in Ref. [15].

We can clearly distinguish three different regions. At distances more than 6.5 Å from the metal surface bulk conditions prevail and the average solvent force on both the ion and the atom vanishes. In the range between 3.5 and 6.5 Å the particles experience a strong repulsive mean force due to the displacement of water molecules from the surface and the concomitant particle loss of the solvation sheath. The magnitude of this force is greater for the ion, which is more strongly solvated than the atom. At very short distances from the surface there are no water molecules between the solute and the metal, and the solvent mean force becomes constant. In this region the force on the ion is negative because the electrostatic interaction with water tends to pull it back towards the solution. In contrast, the atom is expelled from the water and pushed towards the surface, an effect which is familiar from the adsorption of uncharged organic molecules on metal electrodes [22].

The same trends are also evident in the solvent contributions to the Gibbs energies of the two solutes, which are obtained from $F_s(z)$ by integration (see Fig. 2(b)). For clarity, the constant of integration was set to zero in the bulk, and so these curves do not reflect the difference in the energies of solvation.

To obtain the total Gibbs energy curves experienced by the ion and by the atom we add the interaction energy of the particles with the metal. Since the molecular dynamics simulations yield only Gibbs energy differences relative to the bulk state, the relative energies of the two bulk levels have to be obtained by going through a cycle that decomposes the reaction $I^- \rightarrow I + e^-$ into a series of steps:

$$\begin{aligned} &I^-(\text{solution}) \rightarrow I^-(\text{above solution}) \\ &\quad \Delta G = -\Delta G_s^r(I^-) \\ &I^- \rightarrow I + e^- \\ &\quad \Delta G = -A \\ &e^-(\text{above solution}) \rightarrow e^-(\text{above metal}) \\ &\quad \Delta G = -e_0(\psi_m - \psi_s) \qquad (2) \\ &e^-(\text{above metal}) \rightarrow e^-(\text{metal}) \\ &\quad \Delta G = -\Phi \\ &I(\text{above solution}) \rightarrow I(\text{solution}) \\ &\quad \Delta G = \Delta G_s^r(I) \end{aligned}$$

In these equations ΔG_s^r denotes the real Gibbs energy of solvation of the species indicated, A is the electron affinity of the iodine atom, ψ_s and ψ_m denote the outer potentials of the solution and the metal at the potential of zero charge (pzc) and Φ is the work function of the metal; 'above' refers to a position in the vacuum just above the indicated phase. All the quantities in Eq. (2) are measurable, but not all are known exactly.

The real Gibbs energy of solvation of the halide ions has been measured by Randles [23], who gives $\Delta G_s^r(I^-) = -2.48$ eV; presumably that of the iodine atom is negligible. The electron affinity of iodide is $A = -3.06$ eV [24]. The work function of Pt(100) is not available, but that of Pt(111) is 5.7 eV and that of polycrystalline platinum is given as 5.65 eV [25]; therefore the latter value should also be a reasonable estimate for the work function of Pt(100). The largest uncertainty lies in the difference in the outer potential between the platinum electrode and the solution at the pzc. The pzc of platinum is rather doubtful; we have taken the value of 0.23 V SHE recommended by Trasatti [26]. The absolute value of the standard hydrogen electrode (SHE) potential on the vacuum scale is controversial; for a good discussion we refer to [27,28]. We prefer the value of 4.7 V, which has been advocated by a number of groups. This results in a value of 0.7 V for the outer potential difference at the pzc of platinum. For comparison we note that a monolayer of water adsorbed on a platinum surface in a vacuum lowers the work function by about 1 V [29]. In view of the fact that the electrochemical experiments are performed at a substantially higher temperature, the lower value obtained here seems reasonable. Going through the cycle of Eq. (2) results in a value of 0.6 eV for the difference between the Gibbs energies for iodine and the iodide ion in the bulk of the solution; owing to the uncertainties in the various quantities, we estimate the error as ±0.2 eV. As expected, the ion is in an energetically more favorable state in the bulk of the solution.

Both particles experience similar Gibbs energy curves as they approach the surface from the bulk (Fig. 3). They pass through a local minimum at a position where they are separated from the surface by one layer of water molecules. This can be interpreted as an adsorption site for a solvated particle. A closer approach to the electrode surface entails a partial desolvation, which requires an energy of activation as the Gibbs energy curves pass through a maximum. This energy barrier contains two contributions: the displacement of water from the metal surface, and the partial loss of the solvation sheaths. The latter contribution is much greater for the ion which attracts the water molecules through Coulomb forces. Hence the energy barrier, defined as the energy difference between the maximum and the local minimum near 6 Å, is higher for the ion (about 0.23 eV) than for the atom (about 0.13 eV). Both Gibbs energy curves show pronounced minima right near the metal surface. The calculated minimum is rather lower for the atom than for the ions. As discussed before, there is only one adsorbed state, and so in reality the two curves merge into one, as indicated in Fig. 1. The curve for the iodine atom has a lower minimum, and so our calculations indicate that the adsorbed state carries a partial charge which is substantially lower than the ionic charge.

Our simulations suggest the following picture for an ion transfer reaction. Before the reaction the ion sits in a weak adsorption site where it is separated from the electrode by one layer of water molecules. As the ion approaches the electrode surface it displaces water from the surface and loses part of its solvation sheath; this requires a substantial energy of activation. Subsequently the ion moves down the Gibbs energy curve towards an adsorption site on the metal surface; simultaneously the electronic interaction with the metal increases, electron exchange is adiabatic and the adsorbed particle generally carries a partial charge.

Therefore the situation is fundamentally different from that for outer-sphere electron transfer reactions. According to the Marcus theory, the reaction coordinate for an electron transfer reaction corresponds to a generalized solvent coordinate. There are two potential energy curves, one for the reduced and one for the oxidized state, both of approximately parabolic shape. The reduction of a molecule occurs in the following way. A thermal fluctuation excites the oxidized state and takes the system to the crossing point of the two potential energy surfaces (Fig. 4) where it takes up an electron. Subsequently the system relaxes to its new equilibrium position on the potential energy curve for the reduced state. Therefore the electron transfer is caused by a solvent fluctuation and not by the movement of the redox couple. The electron transfer occurs at the intersection of the two Gibbs energy surfaces. In contrast, the energy of activation for an ion transfer step is not related to an electron exchange with the electrode.

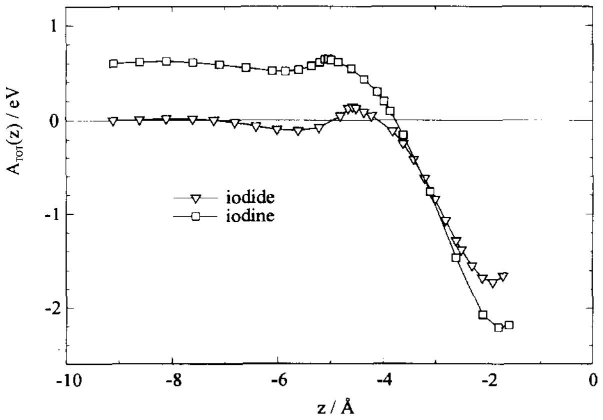

Fig. 3. Total Gibbs energy curves in the absence of an external field.

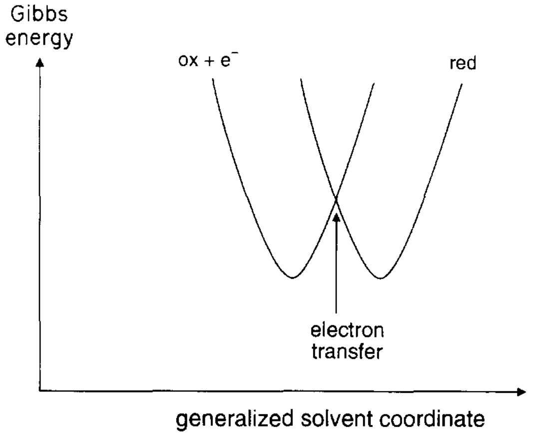

Fig. 4. Gibbs energy curves in the Marcus theory for electron transfer reactions.

Our interpretation is at variance with the recent work of Xia and Berkowitz [13], who assume from the start that there are two different electronic states (ionic and atomic) for iodine adsorbed on a platinum surface and construct Marcus-type Gibbs energy surfaces for these two states from computer simulations. However, even a fairly weak interaction energy (of the order of 0.5 eV) between the adsorbed iodine and the platinum surface leads to the emergence of one partially charged adsorbate state instead of the two charge states which exist in the bulk [18]. Therefore it is difficult to envisage a situation in which an ionic and an atomic adsorbate state would coexist.

3.2. *Results for a charged metal surface*

The rate of an electrochemical ion transfer reaction depends on the electrode potential or, equivalently, the charge density on the electrode surface. Therefore we have performed simulations in the presence of an external electrostatic field *E*. The direction of the field was chosen such that the ion is attracted towards the surface. The resulting Gibbs energy curves are shown in Fig. 5; they have been adjusted to give the same value for the adsorp-

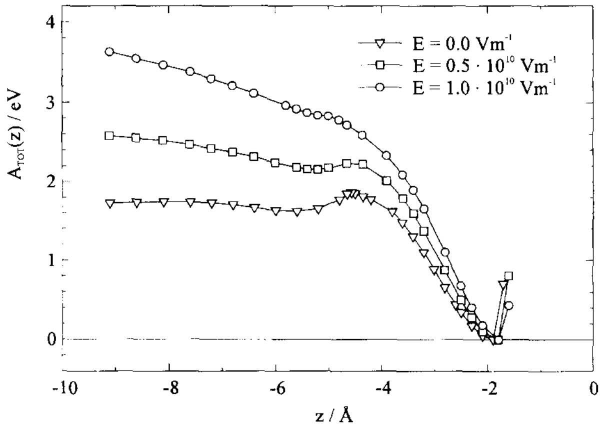

Fig. 5. Total Gibbs energy curves for the iodide ion in the presence of an external field.

tion minimum on the metal surface. Since our ensemble contains only one ion, the external field is not screened by mobile charges and the potential energy of the ion keeps on increasing in the direction towards the bulk of the solution. The presence of an external field substantially lowers the energy of activation required for the adsorption of the ion; at an external field strength of $E = 10^{10}$ V m^{-1} only a vestige of the energy barrier is left.

These changes in the Gibbs energy curves are caused by both the direct contribution $e_0 E$ of the external field to the potential energy of the ion and the restructuring of the solvent in the presence of the field. To separate these two effects we have calculated the mean force exerted by the solvent on the ion. For a classical dielectric continuum with a dielectric constant ϵ this force has a bulk value of magnitude $e_0 E(1 - 1/\epsilon)$. Owing to the finite size of our simulation cell we do not quite reach a constant bulk value, but the variation is small near the center of our simulation box. Therefore we have subtracted the value of the force at the center and plotted the remaining force in Fig. 6(a). The mean solvent force pushes the ion back towards the bulk of the solution. It shows a pronounced minimum at a distance of about 5 Å from the top layer of the metal atoms. This is also evident from the corresponding Gibbs energy curves obtained by integration (Fig. 6(b)). This solvent force has the greatest magnitude in the absence of an external field, and decreases with increasing field strength. The external field tends to align the water molecules with their dipole moments perpendicular to the metal surface [30]. This interferes with the formation of a solvation cage around the ion, which is therefore weaker in the presence of a field, and hence the mean solvent force is reduced near the surface.

To investigate this effect further we have also calculated the mean solvent force for the iodine atom (Fig. 7). Somewhat to our surprise, the absolute value of the force at the minimum is also smaller in the presence of an external field. Apparently, the field weakens the hydrogen-bonded water structure and thus reduces the

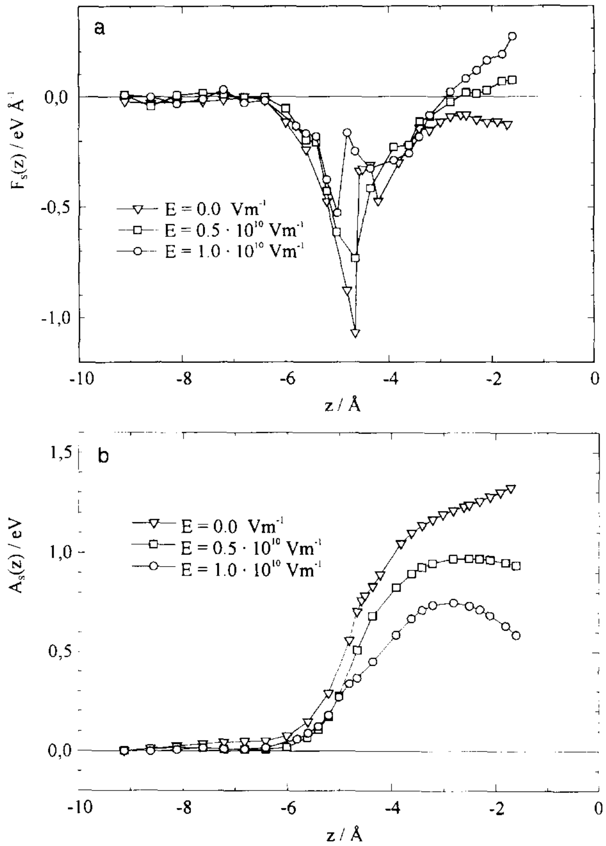

Fig. 6. Mean solvent force acting on the iodide ion; the bulk part has been subtracted (see text).

solvent force on the atom. However, in a real system the electric field will be inhomogeneous and attract the water molecules towards the surface. This will counteract the weakening of the water structure, and so it is not clear whether the trend observed in Fig. 7 will persist in more realistic models.

Electrochemical ion transfer reactions are usually performed in solutions with a high concentration of supporting electrolyte which shields the external field. The resulting changes in the potential energy profile will affect the

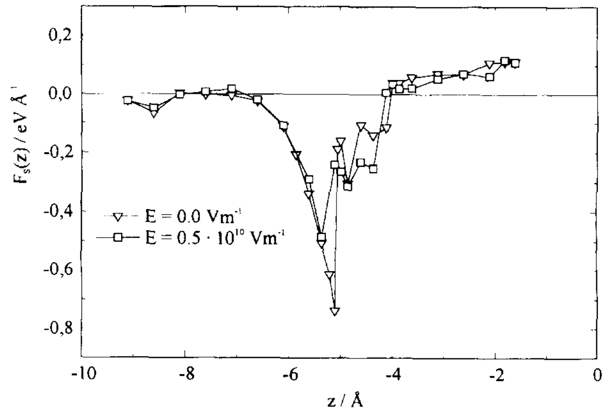

Fig. 7. Mean solvent force acting on the iodine atom.

Gibbs energy curves for the ions. The greatest changes will be in the bulk, where the Gibbs energy will attain a constant value, and in the region about one Debye length from the surface. The screening will be less effective right at the interface, and so we expect the changes caused by the external field to remain qualitatively similar in this region.

4. Conclusion

Our simulations indicate that the rate of ion transfer in aqueous solutions is determined by the displacement of water from the metal surface and the concomitant partial desolvation of the transferring ion. The electron transfer and partial discharge of the ion occurs after the water has been displaced and does not influence the energy of activation. The iodide ion, for which our simulations were performed, has a relatively small solvation energy. Therefore we should expect the same mechanism to operate for the transfer of other ions, and the effect of the solvent will often be even stronger.

This mechanism may also explain why the Butler–Volmer law of Eq. (1) holds approximately for ion transfer reactions. According to our model, the rate-determining step is the passage from the weakly adsorbed state, where one layer of water separates the ion from the metal, to the position right on the metal surface. In concentrated solutions a change $\Delta\phi$ in the electrode potential will alter the Gibbs energy change for this step approximately by an amount $ze_0\Delta\phi$, as is assumed in the phenomenological derivation of the Butler–Volmer law. Changing the electrode potential changes the field, and hence the energy barrier, which can be described formally by a transfer coefficient. However, since the energy of activation is determined by the restructuring of the solvent, it should change with temperature. Therefore this model predicts a transfer coefficient which depends on temperature.

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